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# Low energy ion beam induced changes in structural and thermal properties of polycarbonate



Radiation Physics and Chemistry

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#### HIGHLIGHTS

- Ion irradiated of polycarbonate to improve those thermal and mechanical properties.
- The temperature of decomposition is increase from 495.49 °C to 512.33 °C.
- The tensile strength is increase from 9.30 MPa to 16.20 MPa for irradiated samples.
- The Elongation is decreases by increasing ion fluence.
- The stress is increase by increasing ion fluence.

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#### ABSTRACT

The aim of the present study is extended for obtaining relation between the collision of ion beam with polycarbonate polymer (PC) and the introduced modification of technological applications. Polycarbonate films are irradiated by a 6 keV argon ion beam extracted from locally design cold cathode ion source with different ion fluences. The films are characterized using X-ray Diffraction (XRD), Mechanical tester, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The increase in ion beam irradiation leads to an increase in the tensile strength and reduction in elongation at break for PC. TGA Analysis shows that the thermal decomposition temperature of irradiated polycarbonate changes with ion fluence. The DSC graphs show improvements in thermal stability with increase in the activation energy after ion beam irradiation. Ion penetration depths and distributions of scattered atoms are calculated using SRIM Monte Carlo simulation programs.

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#### 1. Introduction

Surface modification of polymers has become an important field of research which stimulated numerous efforts. An ion beam treatment of a polymer causes a significant transformation of the structure and properties of the modified samples (Jung et al., 2010). The penetrating ions in the target cause collisions with electrons and atoms of the target molecules. As a result of these collisions, the atoms and electrons can be shifted from their equilibrium positions, leading to the excitation of vibrational modes and the resulting phonons propagate to dissipate the energy (Kondyurin and Bilek, 2015). If the recoiled atoms or electrons have enough kinetic energy, they will interact in the same way

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with other atoms and electrons of the target, transferring energy in the process, in this way, generating cascades of collisions (Abdul-Kader, 2013). In other words, irradiated polymers can changes the physical properties for polymer such as convert them from insulators to good electrical conductivity materials that are a good sign and making these materials can be used in various electronic applications (Raghu et al., 2014). Ion bombardment induces formation and transport of reactive species, which are able to permanently change the electronic and chemical properties of polymers (Tayel et al., 2015). Ion beam irradiation deposits energy inside the target material that causes irreversible modifications in its structure at the macromolecular scale. The effectiveness of these changes produced in the polymers depends on the structure of the polymer along with the experimental conditions of ion bombardment like ion energy, fluence and beam current. The interaction of the ions with polymer leads to bond breaking, formation of free radicals and various phenomena that are induced

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by the complex secondary chemical processes along the trajectory of the ions (Wang, 2000). The ionization and electronic excitation processes are known to lead in polymers to both, chain scission and cross-linking, their ratio depending on the system. Chain scission leads to decreasing molecular weight and cross-linking to its increase. Both effect changes the polymer phase, chemical structure, crystallinity and the molecular weight (Sun et al., 2003). In the recent few years, studies related to irradiation effects on polymers have emerged as an important area of basic as well as applied research (Atta et al., 2013; Abdel-Galila et al., 2013). Irradiation of polymer processing methods have emerged such as radiation assisted diffusion, growth of polymer nano-composites, polymer blends, polymer grafting etc. (Cleland et al., 2005; Chmielewski Andrzej et al., 2005). Ionizing radiation processing, using ion beam, electron beam, gamma-rays and X-ray has been demonstrated on a large commercial scale to be very effective means of modifying end-use properties of different polymers (Siddhartha et al., 2012; Kumar et al., 2012a; Siljegović et al., 2011; Abdel Moez et al., 2012). Owing to its chemical and thermal stability, Polycarbonate has been widely used for filtration and nanowire or nano-tube synthesis applications with the through-film hole created by the ion-track etch process (Apel, 2001; Chakarvarti, 2009; Muench et al., 2011; Toimil Molares et al., 2001). Chain scission has occurred for PC irradiated with Li<sup>7</sup> ion beam fluence equals 10<sup>12</sup> ions.cm<sup>-2</sup>, while the end linking has occurred at the ion fluence equals  $5 \times 10^{12}$  ions cm<sup>-2</sup>, and with Ni<sup>59</sup> ion fluence equals  $10^{12}$  ions cm<sup>-2</sup> (Mujahid et al., 2004). Some active sites created by scission lead to the intermolecular crosslinking. The degree of ordering of the polymer is dependent on the dose due to the degradation and the cross-linking process (Nouh et al., 2005a,b).

Because the good physical and chemical properties of polycarbonate, such as excellent transparency high compact strength, light weight, heat resistance, stability and it is sterilizable by radiation methods, this makes polycarbonate an advantageous material for several applications such as microelectronics and biosensor production technologies. Aromatics polymer like PC is relatively resistant to ion beam irradiation and is well suited to serve as packaging materials for medical disposables, which are slated to be radiation sterilized. The obtained results, in this work, shed light on the effect of ion beam irradiations of polycarbonate to suitable industrial applications and modify the mechanical and thermal properties through argon Ion beam-induced modifications of the polymer structure. Polycarbonate films are irradiated with 6 keV argon ion beams at different ion fluence ranging from  $0.5 \times 10^{18}$  to  $1.0 \times 10^{18}$  ions cm<sup>-2</sup>. The characterization techniques such as thermo-gravimetric analysis (TGA), X-ray Diffraction (XRD) and mechanical tester were successfully performed to identify the induced changes in physical-chemical properties of the polymer.

#### 2. Experimental procedure

#### 2.1. Sample preparation

The polycarbonate films samples with 100  $\mu$ m thick which were degreased ultrasonically in a dilute detergent solution, rinsed ultrasonically in deionized water, and blown dry in N<sub>2</sub> gas before they were introduced into the chamber. Locally design cold cathode ion source is used for irradiate polycarbonate samples at radiation physics department, National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority. The argon ion beam fluence ranging from 0.5 × 10<sup>18</sup> ions cm<sup>-2</sup> to 1.5 × 10<sup>18</sup> ions cm<sup>-2</sup> using energy, 6 keV.

#### 2.2. Polymer characterization

After irradiation, the samples are characterized by different spectroscopic techniques. The structures are characterized using a fully computerized X-ray diffractometer, Shimadzu XRD-6000, at NCRRT, Cairo, Egypt. XRD patterns in the  $\theta$  range between  $2\theta$  of  $4^{\circ}$  to  $90^{\circ}$  are obtained at a scan rate of  $2^{\circ}$ / min on the diffractometer with CuKa radiation source, a generator voltage of 40 kV, a generator current of 40 mA and a wavelength of 0.1546 nm at room temperature. The thermal analysis are carried out using TGA technique (Shimadzu DTG-60H) and DSC technique (TA. Q20, USA) at National organization for Drug Control and Research (NODCAR), Cairo, Egypt. The mechanical properties including tensile strength (MPa) and elongation at break (%) were tested at room temperature. Every data point is the average of 5 tests. (Mecmesin limited tester, UK), equipped with software. In this system, the different mechanical parameters are calculated directly.

#### 3. Results and discussion

#### 3.1. Modern computer simulation

Modern computer simulation codes, such as Transport of ions in matter (TRIM) and Stopping and Range of Ions in Matter (SRIM), give excellent agreement with experimental data for ion penetration depths, defect distributions, phonon distributions, distributions of scattered atoms and electrons, and transmitted ions (Ziegler, 2006). TRIM and SRIM are based on the Monte Carlo method and are commonly used for simulation of ion implantation effects in solids, including polymers.

Fig. 1 presents the region affected by argon ion track in polycarbonate calculated with the SRIM code. The argon ion penetrates into the polycarbonate, colliding with carbon and hydrogen atoms, and they recoil. The recoiled atoms receive energies high enough to leave their sites in the structure and subsequently collide with other carbon and hydrogen atoms. A tree of collisions ions implanting into randomly distributed target atoms are shown in the figure to achieve a statistical understanding of these events. The final distribution of the positions for the implanted ions come to rest (stopped ions) has a maximum under the modified surface layer as shown in Fig. 2.

#### 3.2. Ion source operating parameters

The output characteristics of the ion source are obtained as shown Fig. 3. The operating condition of the ion source in this experiment are, Ar ion beam  $I_b$ =100 µA, ion energy is 6 keV, pressure =2 × 10<sup>-4</sup> mbar and different time collision.

#### 3.3. X-ray diffraction measurements for PC

The diffraction pattern of pristine PC film shows a peak at  $2\theta$  equals  $17.2^{\circ}$  and the full width at half maximum (FWHM) gets progressively broader, this behavior may be associated with the decrease in crystallinity of the polymer (Kumar et al., 2012b). Fig. 4 shows a slightly decrease in the intensity of the main peak after ion beam irradiation. Some of these changes have been attributed to the cross-linking of the polymer chains by incident ion beam radiation. Where, the ion beam irradiation leads to break the covalent bonds, formation of carbon clusters, liberation of radical species and formation of some new chemical bonds (Kumar et al., 2011). The existence of amorphous portion leads to the appearance of characteristic amorphous halos in the diffraction pattern. The outward appearance of a transition from amorphous polycarbonate to crystalline material is generally a change in

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